



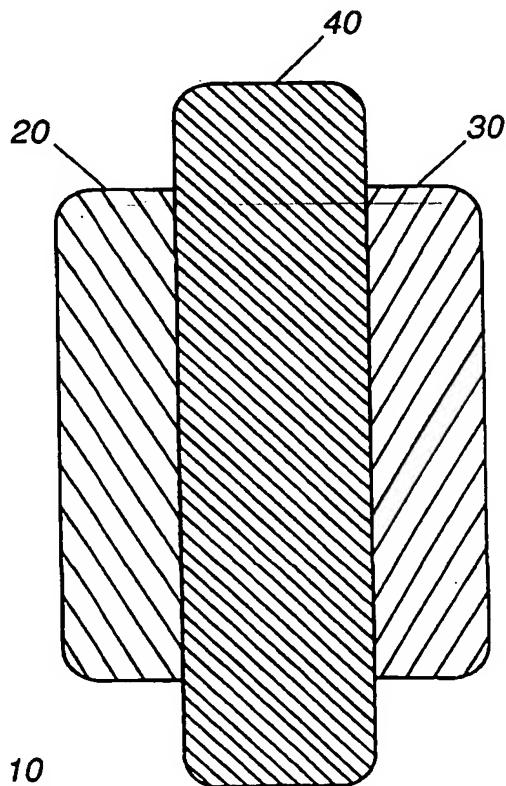
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(54) Title: IMPROVED ELECTRODE MATERIAL FOR AN ELECTROCHEMICAL CELL AND METHOD OF MAKING SAME

(57) Abstract

A method for preparing a lithiated transition metal oxide electrochemical charge storage material for use in an electrochemical cell. The cell (10) includes a cathode (20), an anode (30) and an electrolyte (40) disposed therebetween. The method involves the preparation of the lithiated, transition metal oxide material in an inert environment. The materials are characterized by improved electrochemical performance, and a multiphase composition in which at least one phase is substantially crystalline, while a second phase is substantially amorphous.



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IMPROVED ELECTRODE MATERIAL FOR AN ELECTROCHEMICAL CELL AND METHOD OF MAKING SAME

Cross Reference to Related Applications

5 This application is a continuation-in-part of U.S. application Serial No. 08/663,415, filed June 17, 1996, by Zhenhua Mao, entitled "IMPROVED ELECTRODE MATERIAL FOR AN ELECTROCHEMICAL CELL AND METHOD OF MAKING THE SAME" and assigned to Motorola, Inc.

10 Technical Field

This invention relates in general to secondary rechargeable electrochemical cells, and more particularly to secondary lithium electrochemical cells having high capacity positive electrodes.

15 Background of the Invention

Secondary lithium electrochemical cells and particularly lithium batteries, using an intercalation compound as the positive electrode or cathode of the battery have been studied intensely during the past decade. Heretofore, the cathode material used in these batteries was typically a 20 lithiated cobalt oxide, nickel oxide, or manganese oxide. Lithiated transition metal oxide batteries are being studied as an alternative to current nickel-cadmium and nickel-metal hydride cells because they possess several attractive characteristics, e.g. high cell voltage, long shelf life, a wide operating temperature range, and use of relatively non-toxic materials. The 25 earliest reports of lithiated nickel oxide and lithiated cobalt oxide materials as positive electrode materials in rechargeable lithium batteries occurred more than a decade ago and is shown in, for example, U.S. Patent Nos. 4,302,518 and 4,357,215 both to Goodenough, et al.

These materials have been intensively investigated and one of them, 30 lithium cobalt oxide is currently used in commercial lithium ion batteries. Numerous patents have been issued for different improvements in these materials as the positive electrode for lithium cells. An example of a recent improvement is illustrated in U.S. Patent No. 5,180,547 to VonSacken for "HYDRIDES OF LITHIATED NICKEL DIOXIDE AND SECONDARY CELLS PREPARED THEREFROM". The VonSacken reference teaches fabricating 35 the hydroxides of lithium nickel dioxide fabricated in an atmosphere

including a partial pressure of water vapor measuring about 2 torr. Regardless of the materials used in such cells, each material is synthesized in an oxidizing environment such as O₂ or air using nickel or cobalt and lithium containing salts. For example, a publication to Ohzuku, et al 5 published in the Journal of the Electrochemical Society, Vol. 140, No. 7, July 19, 1993, illustrates at Table I thereof the special processing methods for preparing lithiated nickel oxide. Each of the methods illustrated in the Ohzuku, et al reference show preparing the material in an oxidizing environment of either oxygen or air.

10 Charge and discharge of the materials fabricated according to these processes proceeds by a charge mechanism of deintercalation and intercalation of lithium ions from and into these materials. The materials synthesized by the prior art methods have a reversible capacity on the order of approximately 135 milliamperes (mAh/g). In other words, about 0.5 15 lithium ions can be reversibly deintercalated and intercalated from and into each mole of lithiated nickel oxide or lithiated cobalt oxide.

A significant amount of the capacity of these materials resides at potentials higher than about 4.2 volts versus lithium. If more than 0.5 20 lithium ions is removed from each of either lithiated nickel oxide or lithiated cobalt oxide, potentials higher than 4.2 volts versus lithium are required causing decomposition of most electrolytes. Further, removal of more than 0.5 lithium ions will result in irreversible changes to the 25 structure of these materials, causing a decrease in the capacity during charge and discharge cycles. This result was reported in a publication by Xie, et al, presented at the Electrochemical Society Fall Meeting, 1994, Extended Abstract No. 102, Miami, Florida, October, 1994.

Reversible capacities of the most commonly used materials synthesized in O₂ and air atmospheres are very sensitive to residual, active 30 lithium salts, such as Li₂O, LiOH, and LiCO₃, each of which result from the synthesis process. Moreover, the prior art processes tend to result in a single phase crystalline material, such as a single phase crystalline lithiated nickel oxide material. It is hypothesized that these artifacts of the prior art preparation process result in materials which have lower capacities than might otherwise be expected.

35 Accordingly, there exists a need to develop a new cathode material for rechargeable electrochemical systems which is fabricated of materials that are

relatively environmentally friendly, may be fabricated at low temperatures, and which demonstrate performance characteristics superior to those of the prior art. Such materials should have higher capacity, i.e., greater than about 200 mAh/g at potentials of between 3.0 and 4.2 volts versus a Li metal.

5 Such materials should also have a relatively easy synthesis process which is highly controllable, and which demonstrates insensitivity to residual lithium salts. Finally, the material should have a high initial charge efficiency and be highly reversible charge/discharge reaction so as to provide a material of good cycle life.

10

Brief Description of the Drawings

FIG. 1 is a schematic representation of an electrochemical cell including an electrode in accordance with the instant invention;

15 FIG. 2 is a flowchart illustrating the steps for preparing a lithiated transition metal oxide material in accordance with the instant invention;

FIG. 3 is an illustration of an x-ray diffraction pattern for a first precursor material in accordance with the instant invention;

20 FIG. 4 is a charge, discharge and recharge curve for the lithiated transition metal oxide material fabricated from the first precursor material in accordance with the instant invention;

FIG. 5 is an illustration of an x-ray diffraction pattern for a second precursor material in accordance with the instant invention;

25 FIG. 6 is a charge, discharge and recharge curve for the lithiated transition metal oxide material fabricated from the second precursor material in accordance with the instant invention; and

FIG. 7 is a chart illustrating discharge capacity versus cycle number for an AA cell with a positive electrode material, in accordance with this invention.

Detailed Description of the Preferred Embodiment

While the specification concludes with claims defining the features of the invention that are regarded as novel, it is believed that the invention will be better understood from a consideration of the following description 5 in conjunction with the drawing figures, in which like reference numerals are carried forward.

Referring now to FIG. 1, there is illustrated therein a schematic representation of an electrochemical cell 10 including a lithiated transition metal oxide electrode in accordance with the instant invention. The 10 electrochemical cell includes a positive electrode 20 and a negative electrode 30 and has an electrolyte system 40 disposed therebetween. The electrochemical cell 10 further includes a positive electrode fabricated of a transition metal oxide such as a nickel oxide or a cobalt oxide electrochemical charge storage material which is described in greater detail 15 hereinbelow.

The negative electrode 30 or anode of the cell may be fabricated from a material selected from the group consisting of, but not limited to, lithium metal, lithium alloying metals, such as aluminum, tin, and bismuth, carbon (including graphite and petroleum coke), low voltage lithium intercalation 20 compounds such as TiS₂, V₆O₁₃, MoS₂, and combinations thereof. Alternatively, the negative electrode 30 may be fabricated of the pyrolysis reaction product of multifunctional organic monomers, such as is disclosed in, for example, U.S. Patent Application No. 08/534,427 by Zhang, et al, entitled "Carbon Electrode Materials for Electrochemical Cells and Method 25 of Making Same", filed September 27, 1995; U.S. Patent Application Serial No. 08/600,388, a Divisional Application of 08/534,427, filed February 12, 1996; and U.S. Patent No. 08/561,641 entitled "Improved Carbon Electrode Materials For Lithium Battery Cells And Method of Making Same" filed November 22, 1995, by Zhang, et al; and U.S. Patent Application No. 30 08/534,427 entitled Carbon Electrode Material for Electrochemical Cells and Method of Making Same, filed September 27, 1995, by Zhang, et al, and all assigned to Motorola, Inc.

The electrolyte may be either a solid, a gel, or a liquid electrolyte system. Further, the electrolyte may be either an aqueous or nonaqueous 35 electrolyte system. The electrolyte 40 may also act as a separator between a positive and negative electrodes. In one preferred embodiment, the

electrolyte is fabricated of a material such as is disclosed in commonly assigned copending U.S. Patent Application Serial No. 08/518,732 entitled Blended Polymer Gel Electrolytes in the name of Oliver, the disclosure of which is incorporated herein by reference, as well as U.S. Patent Application 5 Serial No. 08/638,706 entitled Polymer Gel Electrolytes, to Oliver, et al. filed April 29, 1996.

In accordance with the instant invention, there is provided a method for fabricating a lithiated transition metal oxide material which is capable of storing and discharging electrical charge. The material disclosed herein is therefore useful as the cathode in lithium rechargeable batteries. The stabilized material has the formula $\text{Li}_x\text{TM}_y\text{O}_2$, where TM is a transition metal selected from the group of nickel or cobalt and combinations thereof; 10 0.98×1.1 ; and 0.98×1.1 . The electrode material is a multiphase electrode material having at least one phase which is a substantially crystalline phase having the formula LiTM_yO_2 and having a second phase being substantially amorphous. The amorphous phase comprises between 15 10 and 50% of the total electrode material. Other phases of crystalline, microcrystalline, polycrystalline or amorphous material, may also be included in the electrode material. The electrode material may further 20 include one or more modifiers selected from the group of titanium, bismuth, iron, zinc, chromium, and combinations thereof. In one preferred embodiment, the electrode material is LiNiO_2 , and includes a first crystalline phase having the formula LiNiO_2 , and a second substantially amorphous phase which is Li rich as compared to Ni. In this preferred 25 embodiment, the amorphous phase comprises between 20 and 35% of the material.

Referring now to FIG. 2, there is illustrated therein a flowchart of the steps for preparing a lithiated nickel oxide material as described hereinabove. The flowchart 50 illustrates at box 52 the step of providing a 30 first precursor lithium containing material sm1. In a preferred embodiment, the lithium containing precursor material is a nitrate salt and hence is preferably lithium nitrate. Box 54 illustrates the step of providing a second precursor material sm2. The second precursor material is preferably a transition metal hydroxide, and in the embodiment in which the end 35 product is a lithiated nickel oxide, the starting material provided at Box 54 is a nickel hydroxide. This specific nickel hydroxide material can be any one of

a number of a different types of materials, and in one preferred embodiment is an "aged" β -phase nickel hydroxide material. Alternatively, the material provided at Box 54 may be selected from the group consisting of NiO, NiCO₃, Ni(NO₃)₂ · 6H₂O, Ni(OH)₂, CoO, Co(OH)₂, and combinations thereof.

Thereafter, as is illustrated in Box 56 of FIG. 2, is the step of mixing the precursor materials, which can be, for instance, powders or liquid solutions, provided at Boxes 52 and 54. The mixing should be complete, and may be carried out in commonly used mixing devices. Thereafter, the materials are reacted, as by heating, as described in Box 58 of flowchart 50. The conditions and environments in which the heating takes place is important to forming material having a high capacity as illustrated herein. More particularly, the mixed materials are heated in an inert environment. By an inert environment, it is meant that the principal components of the atmosphere in which the heating takes place are not reactive with the precursor materials therein. Accordingly, the heating illustrated in step 58 of Flowchart 50 is carried out in a helium, nitrogen, or argon environment, and the environment in which the heating step 58 occurs is free of oxygen, since the oxygen would react with the precursor materials provided at Boxes 52 and 54.

The heating generates reaction conditions, and preferably takes place in a nitrogen atmosphere at temperatures of about 500-800°C. However, prior to that heating, as is illustrated in Box 58, is the step of preheating the material to a temperature T₁, for a first period of time, X₁. T₁ is typically between about 200-400°C, while R₁ is typically a first rate and is on the order of 2-5° per minute. Alternatively, the mixed precursor material may be placed directly into an oven preheated to T₁, from room temperature. Thereafter, the materials are held at temperature for a period of time, X₁, between approximately 1 and 10 but preferably three hours time. It is important to note that the next step 58 takes places in an inert atmosphere..

After heating at temperature T₁ for period of time, X₁, the material is heated to a second temperature T₂, for a second period of time, X₂. T₂ is typically on the order of approximately 500-650°C, and preferably about 610°C. X₂ is a time period which is typically on the order of between 5 and 40 hours and preferably about 20 hours. The oven is ramped from T₁ to T₂ at a rate of approximately between 1 and 10° per minute, and preferably about 2°

per minute. This heating is maintained under the inert atmosphere described hereinabove with respect to step 58. Optionally, material may be added to the heating at this step and time as is illustrated by Box 62. More specifically, it has been found that if only approximately 80% of the total materials to be reacted by the process illustrated in FIG. 2, are introduced at steps 52 and 54, while the remaining 20% is introduced at Step 62, the reaction products and the performance characteristics of the reaction product are improved.

Thereafter as is illustrated in Box 64, the materials are cooled to room temperature and subjected to a grinding and mixing process which may be carried out in a conventional mill. Thereafter, the materials may be taken from room temperature up to temperature T_3 , which is typically between 600-700°C and preferably about 650°C. Thereafter, the materials are heated in air for a certain period of time X_3 of between 1 and 20 hours and preferably approximately 8 hours. This step is illustrated by box 66 of FIG. 2 and is preferably carried out in an air atmosphere.

Alternatively, after the cooling and grinding steps such as that shown in Box 64, the materials may be introduced into an oven already at temperature T_3 and in an air environment.

Following heating as illustrated in Box 66, the materials are allowed to cool to room temperature by simply removing them from the oven and leaving them in a room temperature environment until the temperature has fallen. This is illustrated at Box 68 of FIG. 2. The invention may be better understood from the examples presented hereinbelow:

25

EXAMPLES

Example I

A mixture of 500 grams (g) of high density spherical "aged" β -phase 30 Ni(OH)_2 and 297g of LiNO_3 was heated at 300°C for 3 hours in He and then heated further at 610°C for 15 hours in He. An additional 74g LiNO_3 was then added to the resulted mixture and mixed/ground. The mixture was then heated at 610°C in He for 15 hours. After that, the material was ground and heated at 650°C in air for 8 hours to form the desired material. The material 35 was then ground and mixed with 6 wt% carbon black and 5 wt% polytetrafluoroethylene (PTFE) and rolled to form a film. A small piece (about

1 cm²) was cut from the film, placed in an experimental cell and tested as the positive electrode. In the experimental cell, Li metal foil was used as the negative electrode, porous polypropylene was used as the separator, and the electrolyte was 1 M LiPF₆ solution in 50% propylene carbonate (pc) and 50% ethylene carbonate (ec).

Referring next to FIG. 3, an X-ray diffraction (XRD) pattern of the preferred high density spherical "aged" β -phase Ni(OH)₂ is depicted. A typical charge, discharge, and recharge curve is presented in FIG. 4, which shows that the material has a capacity of 233 milliamperes hours/gram (mAh/g) within the potential window of 3 to 4.3 volts and an initial charge efficiency of about 94%. Specifically, about 15 mAh/g is lost on the initial discharge. For the same potential window, a material made by a conventional method would have a capacity of less than 200 mAh/g and an initial charge efficiency of less than 86%.

15

Example II

A mixture of Ni(OH)₂ and LiNO₃ was heated in the same manner as in Example I except that the starting material Ni(OH)₂ was "flake" like regular β -phase having an XRD pattern as shown in FIG. 5. As can be seen from comparing the XRD of FIG. 5 with the XRD of FIG. 3, the flake Ni(OH)₂ has a different pattern than the spherical Ni(OH)₂.

A typical charge, discharge, and recharge curve is presented in FIG. 6, which shows that the flake material has an initial capacity of 217 mAh/g, but loses about 30 mAh/g on initial discharge. As shown, the flake material has an initial charge efficiency of 90%.

Example III

A mixture of 500 of spherical "aged" β -phase Ni(OH)₂ and 315g of LiNO₃ was heated in He at 300°C for 4 hours and then heated at 610°C for 15 hours also in He. The resulted material was then mixed with an additional 56g of LiNO₃ and heated in He at 610°C for 10 hours. The material was then ground and heated in air at 650°C for 6 hours. The resulting material was tested as the cathode material in an experimental cell and showed an initial capacity of 228 mAh/g and an initial charge efficiency of 93%.

35

Example IV

A mixture of the material as given in Example I and 6 wt% graphite and 4 wt% polyvinylidene fluoride (PVDF) with N-Methyl-2-Pyrrolidone (NMP) as the solvent was cast on an Al foil and formed into a film. The film was then cut and rolled together with a graphite film as the negative electrode, a 1M LiPF₆ solution in 50% PC and 50% EC as electrolyte and a porous polypropylene as the separator and placed in a steel can conventionally called AA size. The cell was then charged and discharged within the cell voltage window of 2.5 to 4.2 volts at room temperature. FIG. 7 presents the capacity of the cell as a function of cycle number. As shown, the initial capacity of the cell was about 820 mAh. At the 10 25th cycle where the experimental was terminated, 98% of the initial capacity was still retained. AA cells made with equivalent amounts of conventional materials such as LiCoO₂ or LiNiO₂ fabricated by prior art methods as the positive electrode material have a capacity of about 600 mAh. Therefore, this example illustrates that the capacity of AA cells can be increased by greater than 15 30% by using the instant material.

Example V

A mixture of 500 g of Co(OH)₂ and 375g of LiNO₃ was mixed and heated in the following sequence: 300°C for 4 hours and then 610°C for 15 hours. The 20 resulting material was then ground and reheated in He at 610°C for 10 hours, and ground and heated in air at 950°C for 3 hours. The material was then tested as the positive electrode material in an experimental cell in the same manner as in Example I. The material showed an initial capacity of 150 mAh/g within the potential window of 3 to 4.3 volts and an initial charge efficiency of about 25 96%.

Based on the foregoing description, it can be understood that the lithiated transition metal oxide material fabricated in accordance with the present invention yields superior performance when used as a cathode in lithium rechargeable batteries. To summarize, a mixture of precursor 30 materials, i.e., a lithium containing material and a transition metal hydroxide material, is heated in an atmosphere that does not react with the precursor materials. The atmosphere is preferably oxygen-free and composed of argon, helium, or nitrogen.

The heating of the mixture can occur in one or more steps, and, in a 35 two-step heating process, additional precursor materials can be added at the

second heating step. Thereafter, the materials are cooled, ground, and mixed, preferably in an air atmosphere, to result in the high performance lithiated transition metal oxide.

As mentioned above, use of a spherical "aged" β -phase Ni(OH)_2 having the XRD of FIG. 3 as the transition metal hydroxide material results in a higher capacity lithiated transition metal oxide material than if other transition metal hydroxide precursor material, such as a flake Ni(OH)_2 , is used. It will be appreciated, however, that both of the precursor Ni(OH)_2 materials result in lithiated transition metal oxide material that performs better than lithiated transition metal oxide materials fabricated in conventional manners.

While the preferred embodiments of the invention have been illustrated and described, it will be clear that the invention is not so limited. Numerous modifications, changes, variations, substitutions and equivalents will occur to those skilled in the art without departing from the spirit and scope of the present invention as defined by the appended claims.

What is claimed is:

Claims

1. A multiphase electrode material for a lithium rechargeable electrochemical cell, having an overall formula $\text{Li}_x\text{Ni}_y\text{O}_2$ where $0.98 < x < 1.1$ and $0.98 < y < 1.1$, wherein at least one phase is a substantially crystalline phase having the formula $\text{Li}_x\text{Ni}_y\text{O}_2$, and at least a second phase is substantially amorphous, said amorphous phase comprising between 10-50% of said material.
5
2. A multiphase electrode material as in claim 1, wherein said amorphous phase comprises between 20-35% of said material.
10
3. A method of fabricating a lithiated transition metal oxide electrochemical charge storage material, said method comprising the steps of:
15 mixing a transition metal precursor material and a lithium containing precursor material selected from the group of LiNO_3 , LiOH , Li_2O , and combinations thereof;
heating, for a first time period, said mixture of said transition metal precursor material and said lithium containing precursor material in an
20 inert environment, principal components of which are not reactive with said transition metal precursor material or with said lithium containing precursor material; and
heating said mixture of said transition metal precursor material and said lithium containing precursor material in an oxygen-containing
25 environment for a second time period.
4. A method as in claim 3, wherein said inert environment is selected from the group consisting of Ar , N_2 and He .
30
5. A method as in claim 3, wherein said transition metal precursor material is selected from the group consisting of $\text{Ni}(\text{OH})_2$, $\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, NiO , $\text{Co}(\text{OH})_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CoO , and combinations thereof.
35
6. A method as in claim 3, wherein said transition metal precursor material is a spherical aged β phase $\text{Ni}(\text{OH})_2$.

7 A method of fabricating a lithiated nickel oxide electrochemical charge storage material, comprising the steps of:
mixing a spherical, aged β -phase $\text{Ni}(\text{OH})_2$ with a lithium containing precursor material comprising one or more materials selected from the group of LiNO_3 , LiOH , and Li_2O ; and
5 heating said mixture in an oxygen free environment for a first time period.

8. A method as in claim 7, wherein said oxygen-free environment
10 is selected from the group consisting of Ar, N_2 and He.

9. A method as in claim 7, wherein said heating step includes the further step of subsequently heating said mixture in an oxygen containing environment for a second time period.

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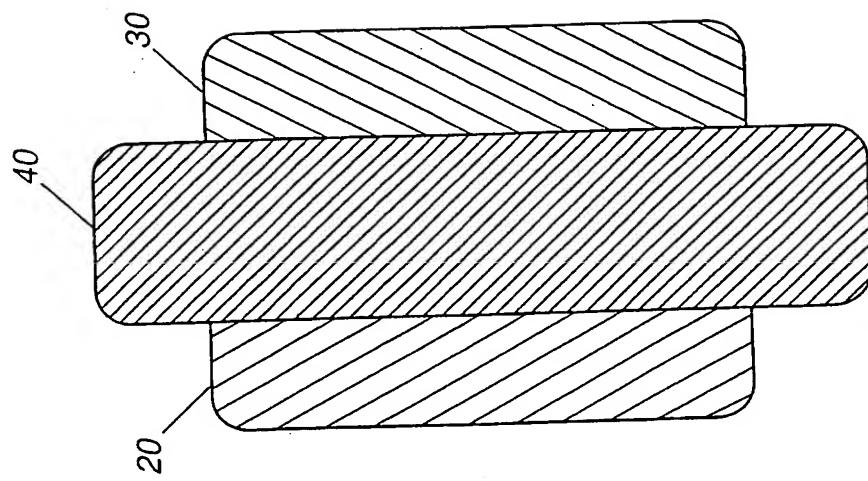


FIG. 1

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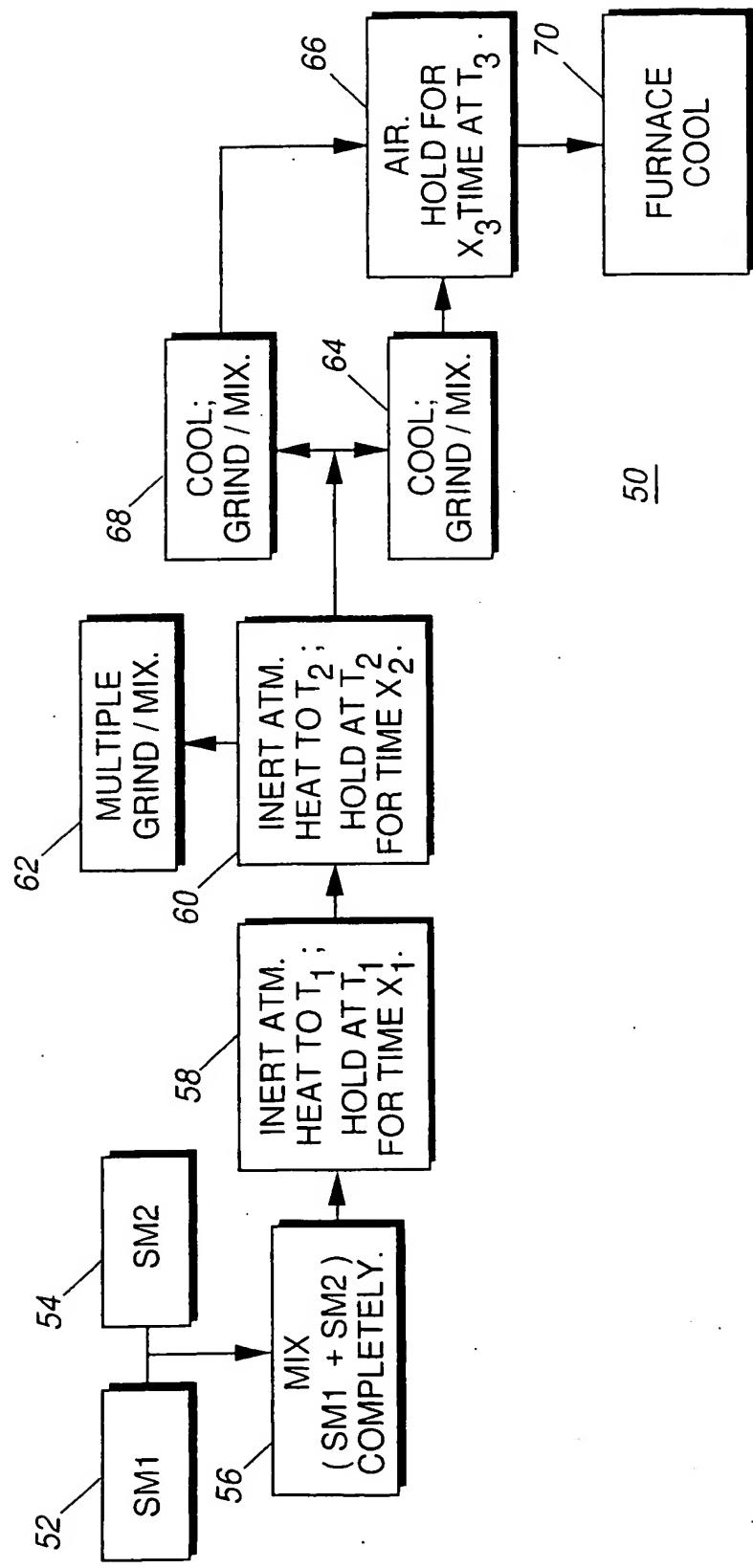


FIG. 2

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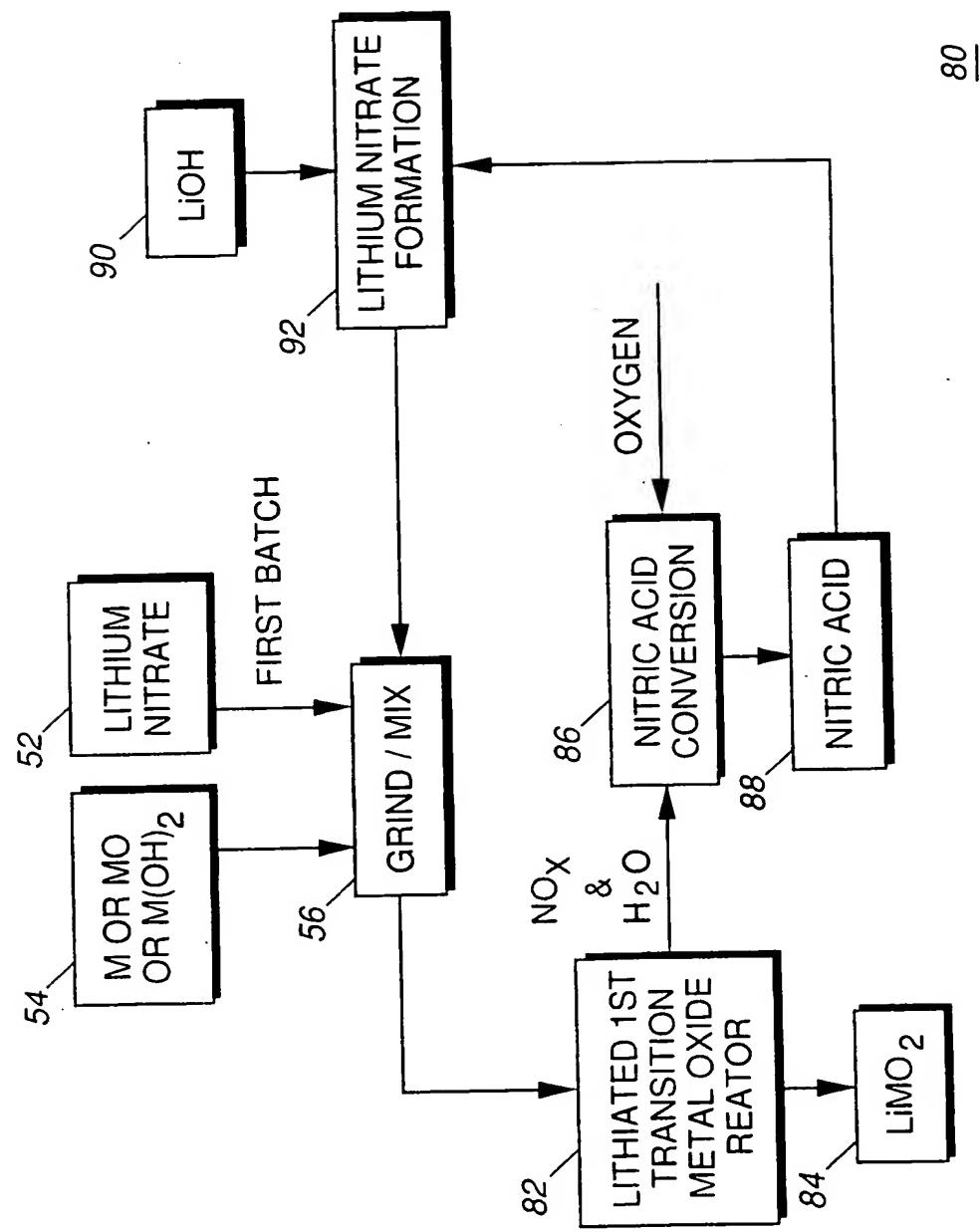


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/12632

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C01G 53/00; H01M 4/32
 US CL :423/594; 429/223

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/594; 429/223

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,264,201 A (DAHN et al) 23 November 1993, col. 7, line 4 to col. 8, line 2, example 1.	1-9
Y	US 5,531,920 A (MAO et al) 02 July 1996, claim 1.	1-9
X ---	OHZUKU, T. Preliminary Results on Synthesis and Characterization of LiCo _{1-x} Ni _x O ₂ (0 < x < 0.5) for 4-Volts Class of Recharable Lithium Cells. Chem. Express. 1990, Vol. 5, No. 10, pp. 733-6.	1-9 -----
Y	PISTOIA, Ct. Lithium Batteries: New Materials, Developments and Perspectives. New York: Elsevier. 1994, Chapter 6, pp. 239-80.	1-9 -----
X ---		1-9
Y		1-9

 Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

23 JULY 1998

Date of mailing of the international search report

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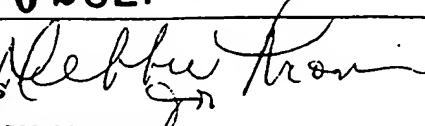
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/12632

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	OHZUKU, T. Electrochemistry and Structural Chemistry of LiNiO ₂ (R3m) for 4 Volt Secondary Lithium Cells. J. Electrochem. Soc. July, 1993, Vol. 140, No. 7, pp. 1862-70.	1-9
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Y		1-9
X	OHZUKU, T. Synthesis and Charaterization of LiNiO ₂ (R3m) for Rechargeable Nonaqueous Cells. Chemistry Express. 1991, Vol. 6, No. 3, pp. 161-4.	1-9
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Y		1-9

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